

REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-98-

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Project (0704-0188).

0604

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE August 1998	3. REPORT TYPE FINAL 3/95-4198
4. TITLE AND SUBTITLE THERMO-OXIDATIVE STABILITY OF POLYIMIDE COMPOSITES FOR AEROSPACE APPLICATIONS		5. FUNDING NUMBERS F49620-95-C-0022 2306/CS 61102F
6. AUTHOR(S) Dr. Chuk L. Leung		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) PolyComp Technologies, Inc. 13963 Recuerdo Drive Del Mar, CA 92014		8. PERFORMING ORGANIZATION REPORT NUMBER PC-OSR-03
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research 110 Duncan Ave., Suite B115 Bolling AFB, DC 20332-0001		10. SPONSORING / MONITORING AGENCY REPORT NUMBER
11. SUPPLEMENTARY NOTES DTIC QUALITY INSPECTED 1		
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited		12b. DISTRIBUTION CODE
13. ABSTRACT (Maximum 200 words) Polyimides are increasingly being used in high-temperature structural composites for airframe and engine applications. A basic understanding of the structure-property relationship of polyimides will enable the intelligent selection and formulation of thermally stable matrices. Our approach aims at developing a understanding of the influence of polymer chemistry on composite stability by conducting novel polymer modifications and formulations to provide different polymer structures to minimize thermo-oxidative degradation of polyimides. We showed that the molecular weights of the prepolymers strongly influence the network structures of the polyimide, and the entrapment of unreacted prepolymer molecules in the polymer network will decrease the thermal stability. We also demonstrated that the network structures of bismaleimides can be modified by inserting bulky substituents around the amic linkages. However, thermo-oxidative stability is not improved because of the tendency for the substituents to undergo scission		
14. SUBJECT TERMS polyimides, composites, bismaleimides, thermo-oxidative stability, polymer network		15. NUMBER OF PAGES
		16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT unclassified
		20. LIMITATION OF ABSTRACT SAR

FINAL TECHNICAL REPORT

1 March 1995 – 28 February 1998

**THERMOOXIDATIVE STABILITY OF POLYIMIDE COMPOSITE
FOR AEROSPACE APPLICATIONS**

Contract No. F49620-95-C-0022

Submitted to

**Air Force Office of Scientific Research
110 Duncan Ave., Suite B115
Bolling AFB, DC 20332-0001**

From

**Chuk L. Leung
PolyComp Technologies, Inc.
13963 Recuerdo Drive
Del Mar, CA 92014**

AUGUST 1998

19980915 040

1. Objectives

Polyimides are increasingly being used in high-temperature structural composites for airframe and engine applications. Various studies have been conducted in an attempt to quantify the isothermal aging effects on these polymer composites. Progress has been made in the understanding of the sample geometryⁱ, reinforcing fibersⁱⁱ, and the temperature effectsⁱⁱⁱ on the thermooxidative stability of the composite as a whole. However, there still exist a need for a systematic study that relates the phenomenological measurement of thermal stability with the chemical structure of the matrix polymers, which are the predominant failure sites, manifested by embrittlement, outgassing, weight loss and microcracking. A basic understanding of the structure-property relationship of polyimides will enable the intelligent selection and formulation of matrices that are thermally stable and would fulfill their mission requirements. Our approach aims at developing a understanding of the influence of polymer chemistry on composite stability by conducting novel polymer modifications and formulations to provide different polymer structures to minimize thermooxidative degradation of polyimides.

2. Status of the Research Effort

To fulfil our objectives, we have investigated and delineated the effects of varying the molecular weights of the polyimide prepolymers, molecular microstructures, and polarity of the functional groups within the microstructure. We have identified parameters that affects (and sometimes improves) the thermooxidative stability of the laminates, as well as factors that do not seem to matter.

We have shown that the network structure of polyimides can be strongly influenced by the molecular weights of the prepolymers. Low prepolymer molecular weight results in a high crosslink density, but due to the presence of entrapped unreacted molecules will lead to lower long-term thermo-oxidative stability of the polymer network. Increasing the molecular weight of the prepolymer lessens the crosslink density and allows as more complete cure, leading to a more thermo-oxidatively stable polymer network.

We also investigated the effects of modifying the molecular structures of the monomers. We hypothesized that by placing bulky substituents adjacent to the reactive sites where chain scission is most likely to occur, the stability of the network can be improved. However, we fail to detect any long-term improvement in the thermo-oxidative stability of the polyimide structures. We believe that at elevated temperatures, the bulky substituents were split off from the polymer chain, essentially reverting the polyimide structures to its un-modified network structure.

We were able, however, to demonstrate that decreasing the polarities of the functional groups adjacent to the imide linkages was effective in improving the stability of the polyimides. We showed that polyimides, in which one of the two carbonyl

functionalities was replaced with non-polar substituents, exhibited lower microcracks and weight loss than the conventional polyimides.

3. Publications

The research effort has been written for publications in technical journals as listed below:

1. C. L. Leung, R. Ghaffarian, and K. Leung, "Thermo-oxidative stability of polyimides – I. Effect of prepolymer molecular weights", *Polymer Degradation and Stability*, **58**, 11-14 (1997). See Appendix A.
2. C. L. Leung and K. Leung, "Thermo-oxidative Stability of Polyimides. Part II: Effect of Molecular Structures", *Polymer Degradation and Stability*, (in press). See Appendix B.
3. C. L. Leung and K. Leung, "Thermo-oxidative Stability of Polyimides. Part III: Effect of Polarity", *Polymer Degradation and Stability*, (submitted). See Appendix C.

4. Professional Personnel Involved

Dr. Chuk L. Leung – Principal Investigator

Mr. Kenneth C. Leung – Researcher

Dr. Eugene Shin – Consultant, Composites Materials and Structures Center, Michigan State University

5. Interactions

A. Papers Presented at Meetings, conferences, seminars

1. C. L. Leung, R. Ghaffarian, "Thermooxidative Stability of Polyimides," Allied Signal Advanced Materials, Santa Clara, CA, March, 1995.
2. C. L. Leung, "Structure-Property Relationship of Polyimides for High Temperature Applications," Sparta, Inc., San Diego, CA, September 1995.
3. C. L. Leung, "Use of High Temperature Polyimides for Electronic Applications," Johnson Matthey Company, Electronics Division, San Diego, CA, February 1996.
4. C. L. Leung, "Effect of Chemical Structures on Thermooxidative Stability of Polyimides," Northrop Aircraft Co., March 1996.

5. C. L. Leung, "High temperature structural composites", Vanguard Composites, San Diego, CA, May 1996.
6. C. L. Leung, "Polyimide as Optical Waveguides," Allied Signal Advanced Materials, Santa Clara, CA, June 1996.
7. C. L. Leung, "Thermooxidative Stability of Polyimide Composite for Aerospace Applications," AFOSR Environmental Stability of Composites Program Review, Anaheim, CA, April 1997.
8. C. L. Leung, "Thermooxidative Stability of Polyimide Composite for Aerospace Applications," *High Temple Workshop XVII*, Naval Postgraduate School, Monterey, CA, February, 1997.
9. C. L. Leung, "Structural-property relationship of Polyimides," Lockheed-Martin, San Jose, CA, March 1997.
10. C. L. Leung, "Thermo-oxidative Stability of Polyimides for Aerospace Applications," *AFOSR Program Review*, Anaheim, CA, April 1996.
11. C. L. Leung, "Thermo-oxidative Stability of Polyimides for Aerospace Applications," *AFOSR Program Review*, Anaheim, CA, May 1997.
12. C. L. Leung, "Thermo-oxidative Stability of Polyimides for Aerospace Applications," *AFOSR Composite Durability Workshop: Joint Workshop between Materials Science and Mechanics Program*, Dearborn, MI, October 1997.

B. Consultative and Advisory Functions to Other Laboratories and Agencies

- Air Force Wright Laboratory, WL/MLBC, on "Hygrothermal Composite Durability and Lifetime Prediction," initiated at June 15, 1996, Dr. D. B. Curliss, WL/MLBCm Wright-Patterson AFB, OH 45433 Tel (937) 255-9078.
- Department of Materials Science & Engineering, University of Michigan, on "Environmental Aging and Initiation of Damage in Advanced Composites," July, with Prof. A. Yee, Department of Materials Sci. Eng., University of Michigan, Ann Arbor, MI, (313) 763-2445.
- Composite Materials and Structures Center, Michigan State University, on "Characterization of Critical Fundamental Aging Mechanisms of High Temperature Polymer Matrix Composites," Prof. R. Morgan, Dr. E. Shin, College of Engineering, Michigan State University, Midland, MI, (517) 839-8505.

- Jet Propulsion Laboratory, on "Processing of PMR-15 Composites," Dr. Cheng Shieh, Materials Branch, JPL, (818)354-8105.
- Air Force Wright Laboratory, WL/MLBC, Dr. Dave Curliss, (937)255-9078.
- Department of Materials Science and Engineering, University of Michigan, May 1997, with Prof. A. Yee, (313) 763-2445.
- University of Western Kentucky, Department of Chemistry, February, 1997, with Prof. Charles W. M. Lee, (502)745-5361.
- Jet Propulsion Laboratory, Applications Engineering Group, February, 1997, on Isothermal Aging of Polyimides, with Dr. R. Ghaffarian, (818) 345-2059.
- Composite Materials and Structures Center, Michigan State University, on Fabrication of Polyimide Composites, with Drs. E. Shin and R. Morgan, (517) 839-8505.
- Purdue University, on "Structure-property relationship of polyimides," Prof. Jim Caruthers, (317) 494-6625.
- NASA Lewis Research Center, on "Structure-properties relationship of polyimides," Dr. James Sutter, (216) 433-3226.
- Prairie View A & M University, on "chemistry of polyimides," Dr. Paul Biney, (409) 857-2222.
- Naval Research Laboratory, on "Processing of Polyimide Composites," Dr. Teddy Keller, February, 1997 (202) 767-3095.
- Indiana State University, on "EPR and Degradation of Polyimides," February 1997, Prof. Yong Ahn, (812) 237-2230.

-
1. Bowles, K. J. and Meyers, A., in *Proc. 31st International SAMPE Symp. and Exhibition*, ed. J. L. Bauer and R. Dunaetz, Soc. for Adv. Mater. and Process Eng., Covina, CA, 1986, p.1285.
 2. Bowles, K. J. and Nowak, G., *J. Composite Materials*, **22** (1988) 966.
 3. Bowles, K. J., *SAMPE Quarterly*, **24** (1993) 49.

APPENDIX A

Thermo-oxidative stability of polyimides—I. Effect of prepolymer molecular weights

Chuk L. Leung, Reza Ghaffarian & Kenneth C. Leung

PolyComp Technologies, Inc., 13963 Recuerdo Drive, Del Mar, CA 92014, USA

(Received 19 April 1996; accepted 13 May 1996)

Thermo-oxidative stability of polyimides under long-term isothermal exposure was studied. Model polyimides of various prepolymer molecular weights were synthesized and fabricated into graphite fiber reinforced composites. These composites were exposed to isothermal aging for up to 6000 h. Dynamic mechanical properties and weight loss measurements indicate that for polyimides prepared from prepolymers with low molecular weight, activation energy for oxidative degradation is decreased, resulting in higher total weight loss in long-term isothermal aging. © 1997 Elsevier Science Limited

1 INTRODUCTION

Polyimides are increasingly being used in high-temperature structural composites for airframe and engine applications. Various studies have been conducted in an attempt to quantify the isothermal aging effects on these polymer composites. Progress has been made in the understanding of the sample geometry,¹ reinforcing fibers,² and temperature effects³ on the thermo-oxidative stability of the composite as a whole. However, there is still a need for a systematic study that relates the phenomenological measurement of thermal stability with the chemical structure of the matrix polymers, which are the predominant failure sites, manifested by embrittlement, outgassing, weight loss and micro-cracking. A basic understanding of the structure-property relationship of polyimides will enable the intelligent selection and formulation of matrices that are thermally stable and would fulfill their mission requirements. Our approach aims at developing an understanding of the influence of polymer chemistry on composite stability by conducting novel polymer modifications and formulations to provide different polymer structures to minimize thermo-oxidative

degradation of polyimides. In this paper, the effect of molecular weights of the prepolymers on the TOS of the cured graphite fiber reinforced polyimide laminates will be examined.

The polyimide samples used in this work are based principally on the formulation commonly found in a commercial polyimide, i.e. PMR-15. The preparation of PMR-15 prepolymers from monomeric reagents has been well described in the literature⁴ and is depicted in Fig. 1. When formulated as shown, the prepolymer has a molecular weight of about 1500 (abbreviated as 15). During cure, a polymer network is formed by polymerization and crosslinking of the norbornene endgroups in a reverse Diels–Alder reaction.⁵ Therefore, the network crosslink density and molecular weight between the crosslinks are determined by the molecular weights of the prepolymers.

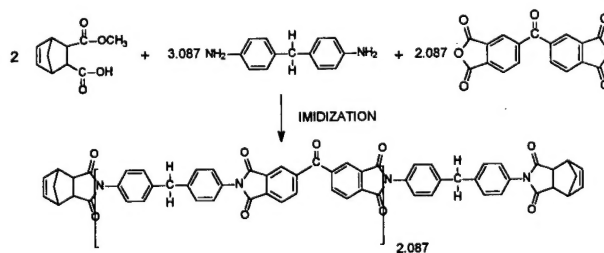


Fig. 1. Synthesis of PMR-15 prepolymer.

2 EXPERIMENTAL

2.1 Materials

3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA) and 4,4'-methylenedianiline (MDA) were purchased from Aldrich Chemicals, Milwaukee, WI. Monomethyl ester of 5-norbornene-2,3-dicarboxylic anhydride (NE) was purchased from Alfa-Aesar, Ward Hill, MA. All chemicals were used as received without further purification. In addition to using the formulation for commercial PMR-15 (see Fig. 1) with a prepolymer MW of about 1500, we also synthesized experimental prepolymers with varying molecular weights. By incrementally modifying the stoichiometry of the reactants BTDA and MDA, we prepared prepolymers with molecular weights equal to 2400 and 2900, respectively. These are labelled PMR-24 and PMR-29. Prepregs of these experimental prepolymers were prepared by dissolving the respective reactants in tetrahydrofuran and casting onto graphite fabric (8 harness satin, Celion® G30-500 from Fiberite Corp.). The solvent was allowed to evaporate, yielding prepregs with solid content of about 50%.

2.2 Laminate cure

Laminates were obtained by laying up 6-ply of the respective prepregs, each ply measuring 30 cm by 30 cm, placed in a vacuum bag and autoclave cured at 315°C for 6 h. The panels were then post-cured in an air-circulating oven at 315°C for an additional 12 h. Specimens of identical dimensions, 20 cm × 20 cm, were cut from the panels and edge polished.

2.3 Isothermal aging

Thermal exposure was carried out in an air-circulating Blue M oven at atmospheric pressure. Specimens, each measuring 20 cm × 20 cm, were previously dried at 150°C for 24 h before their initial weights were determined. The weighed panels were then arranged vertically in the oven, with care being taken to minimize dead-spots in air circulation. At pre-determined time intervals, the oven heater was turned off, and the temperature was allowed to return to ambient. The panels were then removed from the oven and stored in dessicators while waiting to be weighed.

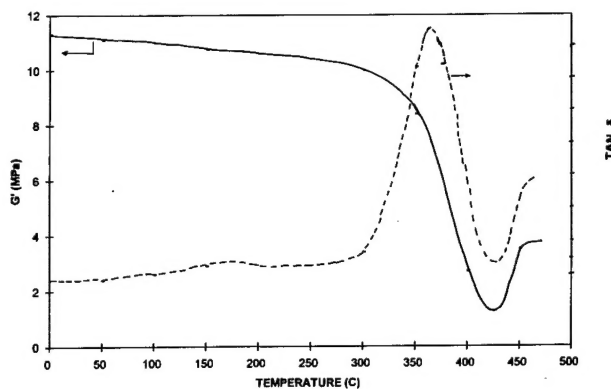


Fig. 2. DMA of PMR-15.

2.4 Dynamic mechanical analysis

From each post-cured panel, a specimen measuring 1 cm × 10 cm was cut and used to measure the dynamic mechanical properties on a DuPont DMA instrument at an amplitude (p-p) of 0.20 mm. A temperature scan of 5°C/min from room temperature to 450°C was used.

3 RESULTS AND DISCUSSION

The dynamic mechanical properties of the three formulations are shown in Figs 2–4. The data show that the specimen with the shorter prepolymer molecular weight (PMR-15) specimen exhibits a higher storage modulus (G') than the other two formulations (PMR-24 and PMR-29), indicating a higher crosslink network density. The instrument, however, was unable to resolve any difference in their glass transition temperatures which occurred at about 375°C.

Figures 5–7 shows the weight loss for the polyimide panels as a function of their prepolymer molecular weights when aged at 232, 260 and 315°C, respectively. The data show that up to the first 1000 h of isothermal aging at each

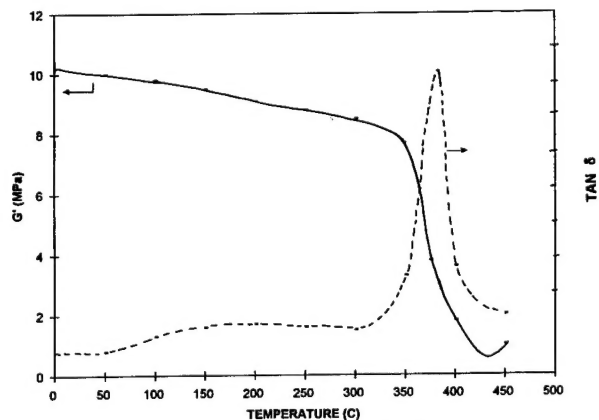


Fig. 3. DMA of PMR-27.

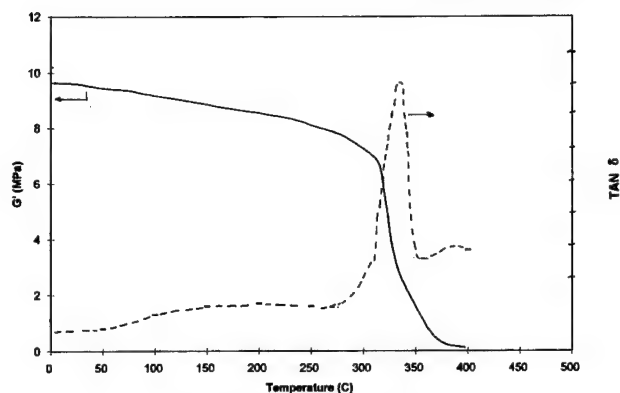


Fig. 4. DMA of PMR-29.

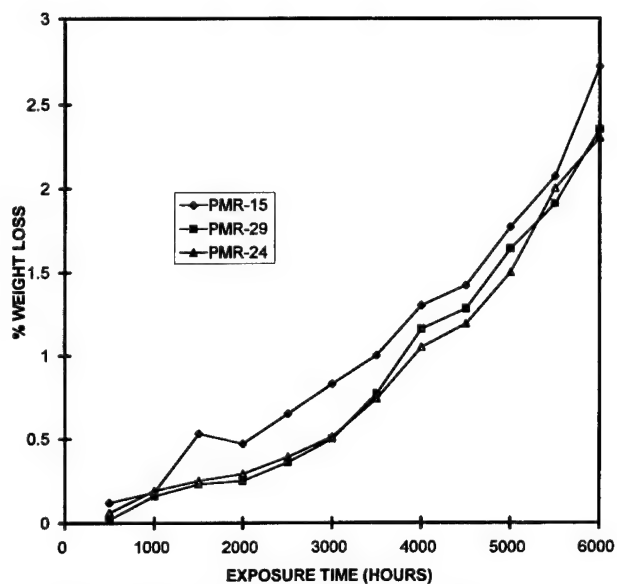


Fig. 5. Weight loss during isothermal aging at 232°C.

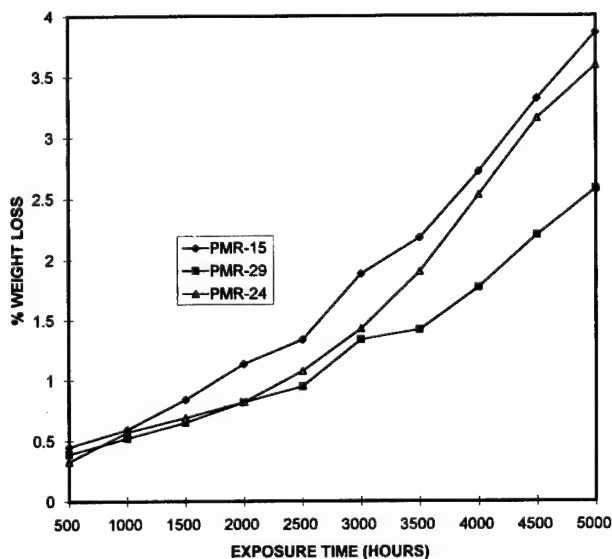


Fig. 6. Weight loss during isothermal aging at 260°C.

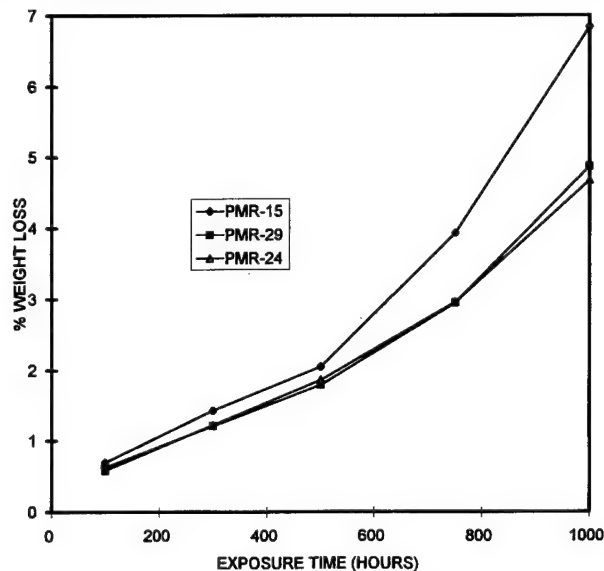


Fig. 7. Weight loss during isothermal aging at 315°C.

temperature, weight loss rate (weight loss per exposure time) is quite linear for each of the three panels. However, as aging time increases, there is a clear separation between the specimens, with the 1500 molecular weight specimen experiencing a higher weight loss rate than the PMR-24 and PMR-29 specimens.

Within the initial linear region, the weight loss data was then fitted to an Arrhenius analysis:

$$W = A \exp(-E_a/RT) \quad (1)$$

$$\text{or } \log W = \log A - E_a/R(1/T) \quad (2)$$

where W = weight loss rate; A = material degradation rate constant; E_a = activation energy; R = universal gas constant; and T = temperature in Kelvin.

A plot of eqn (2), i.e. $\log W$ versus $(1/T)$, is shown in Fig. 8. Analysis of the graphical data is tabulated in Table 1.

The data in Table 1 indicate that activation energy for oxidative degradation due to isothermal aging exposure is lower for the specimen with lower prepolymer molecular weight. Intuitively one would, however, expect that a shorter prepolymer molecular weight would result in a higher crosslinking density with higher thermal oxidative stability. This dilemma can perhaps be overcome by proposing that in a highly cross-linked, rigid network, chain mobility is increasingly being restricted as cure progresses, so that some unreacted fragments remain entrapped within the network. These fragments would be more susceptible to oxidative degradation leading to increased weight loss in long-term aging

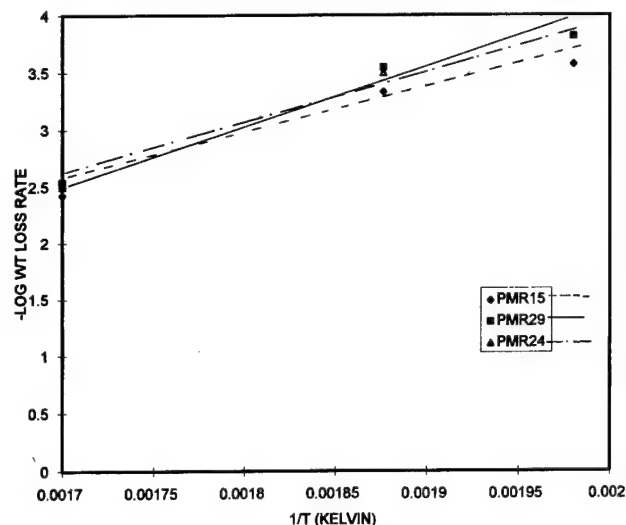


Fig. 8. Arrhenius plot of weight loss versus aging temperature.

conditions. Conversely, a higher prepolymer molecular weight could result in a less restrictive network which allows a more complete reaction between the molecules. This in turn decreases the amount of unreacted fragments, thus lessening thermo-oxidative degradation.

Table 1. Analysis of Arrhenius parameters

Specimen	Slope	E_a (kJ/mol)
PMR-15	4200	40.1
PMR-24	4700	45.0
PMR-27	4800	46.3

4 CONCLUSION

The network structure of polyimides can be strongly influenced by the molecular weights of the prepolymers. A low prepolymer molecular weight results in a high crosslink density, but due to the presence of entrapped unreacted molecules will lead to lowered long-term thermo-oxidative stability of the polymer network. Increasing the molecular weight of the prepolymer lessens the crosslink density and allows a more complete cure, leading to a more thermo-oxidatively stable polymer network.

ACKNOWLEDGEMENT

This work is supported by the U.S. Air Force Office of Scientific Research under Contract F49620-95-C-0022.

REFERENCES

1. Bowles, K. J. & Meyers, A., in *Proc. 31st Int. SAMPE Symp. and Exhibition*, ed. J. L. Bauer and R. Dunaetz. Soc. for Adv. Mater. and Process Eng., Covina, CA, 1986, p.1285.
2. Bowles, K.J. and Nowak, G., *J. Compos. Mater.*, 1988, **22**, 966.
3. Bowles, K.J., *SAMPE Quarterly*, 1993, **24**, 49.
4. Serafini, T.T. and Delvigs, G.R., *J. Appl. Polym. Sci.*, 1972, **16**, 905.
5. Lubowitz, H.R., *ACS Org. Coat. Plast. Chem.*, 1971, **31**, 561.

APPENDIX B

Thermooxidative Stability of Polyimides. Part II: Effect of Molecular Structures

Chuk L. Leung and Kenneth C. Leung

PolyComp Technologies, Inc., Del Mar, CA 92014, USA

Abstract

Thermooxidative stability of polyimides under long-term isothermal exposure was studied. Model polyimides with novel chemical structures were synthesized to delineate the effects of molecular structures on weight loss upon aging at elevated temperatures. Results indicate that for polyimides with bulky side groups, there was an initial lessening of weight loss. However, long-term aging show that the bulky substituents eventually exacerbate the degradation of the polyimide composites.

Thermooxidative Stability of Polyimides. Part II: Effect of Molecular Structures

Chuk L. Leung, and Kenneth C. Leung

PolyComp Technologies, Inc., Del Mar, CA 92014, USA

1. INTRODUCTION

Polyimides are increasingly being used in high-temperature structural composites for airframe and engine applications. Various studies have been conducted in an attempt to quantify the isothermal aging effects on these polymer composites. Progress has been made in the understanding of the sample geometry¹, reinforcing fibers², and the temperature effects³ on the thermooxidative stability of the composite as a whole.

However, there still exist a need for a systematic study that relates the phenomenological measurement of thermal stability with the chemical structure of the matrix polymers, which are the predominant failure sites, manifested by embrittlement, outgassing, weight loss and microcracking.. A basic understanding of the structure-property relationship of polyimides will enable the intelligent selection and formulation of matrices that are thermally stable and would fulfill their mission requirements. Our approach aims at developing a understanding of the influence of polymer chemistry on composite stability by conducting novel polymer modifications and formulations to provide different polymer structures to minimize thermooxidative degradation of polyimides. In the previous paper⁴, we showed that the network structure of polyimides can be strongly influenced by the molecular weights of the prepolymers. A low prepolymer molecular weight results in a high crosslink density, but due to the presence of entrapped unreacted molecules will lead to decreased long-term thermooxidative setabiilty of the polymer network. Increasing the molecular weight of the prepolymer lessens the crosslink density

and allows a more complete cure, leading to a more thermooxidatively stable polymer network. In this paper, we wish to explore the effect of modifying the chemical structures of the imide moieties, in the hope that degradation by chain scission will be minimized.

Through the identification of decomposition products, Ehlers *et al.*⁵ proposed a mechanism for the degradation of polyimides.

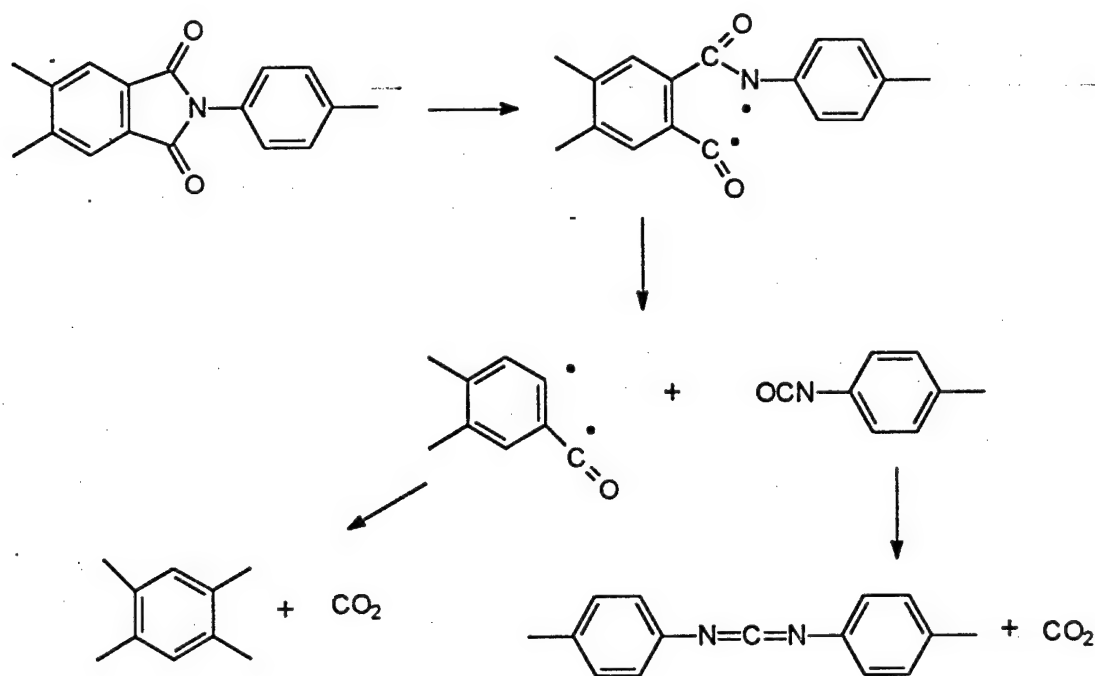


Figure 1. Proposed thermooxidative decomposition mechanism for polyimides

As shown in Figure 1, they proposed that the initiation reaction consists of homolytic cleavage of the imide ring, which is probably the rate determining step. When a polymer chain is thermally cleaved without an initiator, a cage effect is observed for the separation of a pair of polymer radicals produced by main-chain scission in the cage^{6,7}. There are

two possible processes by which chain scission can be made permanent: first by translational diffusion of radicals, second by segmental diffusion of radical-containing polymer chain ends away from each other. As chain entanglement, crosslinking, or conformational rotation barrier increase, both types of diffusion become highly restricted, leading to possible recombination, or "self-healing", of broken chains.

We attempt to test this postulation and investigate the efficacy of amplifying the cage effect by incorporating bulky substituents close to the imide bonds. We hypothesize that the steric hindrance created by these bulky substituents in close proximity to the labile amic radicals will similarly inhibit their mobility, so that cage recombination can be enhanced. These novel monomers are depicted in Figure 2.

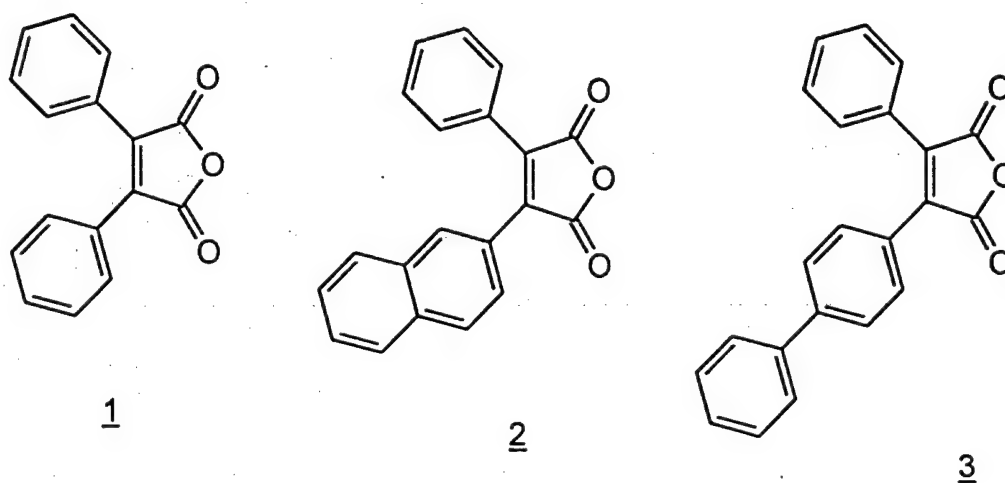


Figure 2. Chemical Structures of Polyimide Precursors with Bulky Substituents

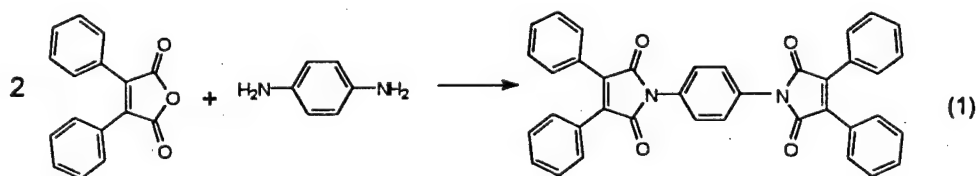
2. EXPERIMENTAL

2.1 Monomer Synthesis

Substituted maleic anhydrides (1), (2), and (3) were prepared by a Perkin condensation of benzoylformic acid as the mixed K-Na salt with the respective phenyl-, 1-naphthyl-, or 4-biphenyl-acetic acid in acetic anhydride, as first described by Koelsch and Wawzonek⁸ and later expanded by Fields *et al.*⁹. A typical synthesis for dianhydride (1) is described here. A mixture of 13.6 g (0.1 mol) of phenylacetic acid, 18.8 g (0.1 mol) of potassium benzoyl formate, and 200 ml of acetic anhydride was stirred and heated at 90-95°C for 4 hours. The cooled solution was poured into stirred 1.5 L of water to decompose the acetic anhydride. The precipitate was collected, dried, and recrystallized from acetone to give 85% of (1), m.p. 146-149°C (lit.: 149-152°C). The m.p. for (2) is 162-165°C (lit.: N. A.), and for (3) is 157-161°C (lit.: N. A.).

Preparation of bismaleimide monomers

Bismaleimide monomers were prepared by reacting the respective diamine and anhydride in 1:2 molar ratios in either tetrahydrofuran or dimethylformamide, such as depicted in Scheme (1):



The crude BMI monomers were isolated by precipitating into methanol, and purified by recrystallizing from toluene. By using combinations of various diamines and anhydrides, a large number of bismaleimide monomers with varying degrees of steric and shielding effects, as shown in Figure 3, were prepared in sufficient quantities for

prepregging. For comparison, a state-of-the-art bismaleimide resin, Matrimid® 5292 from Ciba Geigy Corp was used as baseline.

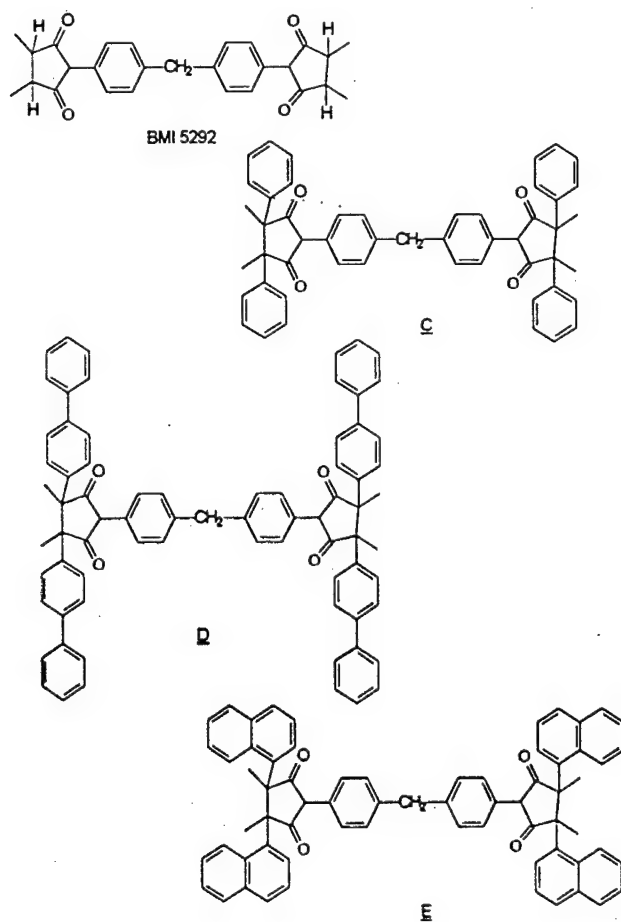


Figure 3. Candidate BMI Monomers

2.2 Prepregging

Pure bismaleimides are brittle polymers and need to be formulated with other monomers or oligomers to impart processibility and mechanical strengths to the laminate. O-o'diallyl bisphenol A (BPA) reacts with bismaleimide via an "ENE" type chain extension reaction, and is used in several commercial BMI formulations. Equimolar amounts of the respective BMI monomers and BPA were dissolved in THF or THF/DMF and used to

impregnate Amoco T650-35 8HS graphite fabrics. The solvent was allowed to evaporate to near dryness to obtain prepregs with resin content of about 40-45%. Prepregs were cut into appropriate sizes and eight-ply layups were prepared.

2.3 Laminate Cure

The lay-up was vacuum-bagged and cured in a heated press. The cure cycles were determined by prior measurements of the differential scanning calorimetry of the formulations. A typical cure cycle (e.g. monomer C) is as follows:

1. Put prepreg in cold press, apply kissing pressure
2. Heat press at 5-7°C/min from room temperature to 250°C
3. Dwell at 250°C for 1 hour, slowly apply 100 psi pressure
4. Cure at 250°C for 6 hours
5. Turn off heater and let laminate cool to room temperature under pressure
6. Debag and trim.

2.4 Isothermal Aging of Composite Laminates

Laminate specimens, each measuring 10 cm by 10 cm, were predried in vacuum oven at 100°C for 24 hours and then stored in a dessicator until use. Pre-weighed specimens were placed in air-circulating oven at 260°C and were weighed at regular intervals.

3. Results and Discussion

Figure 3 shows the microstructures of the bismaleimide polymer matrices. It can be clearly shown that the electronic environments around the imide ($C=O$ and $C-N$) bonds are different for each polymer. Figure 4 shows the cumulative weight loss of these laminates at 260°C, up to 5000 hours.

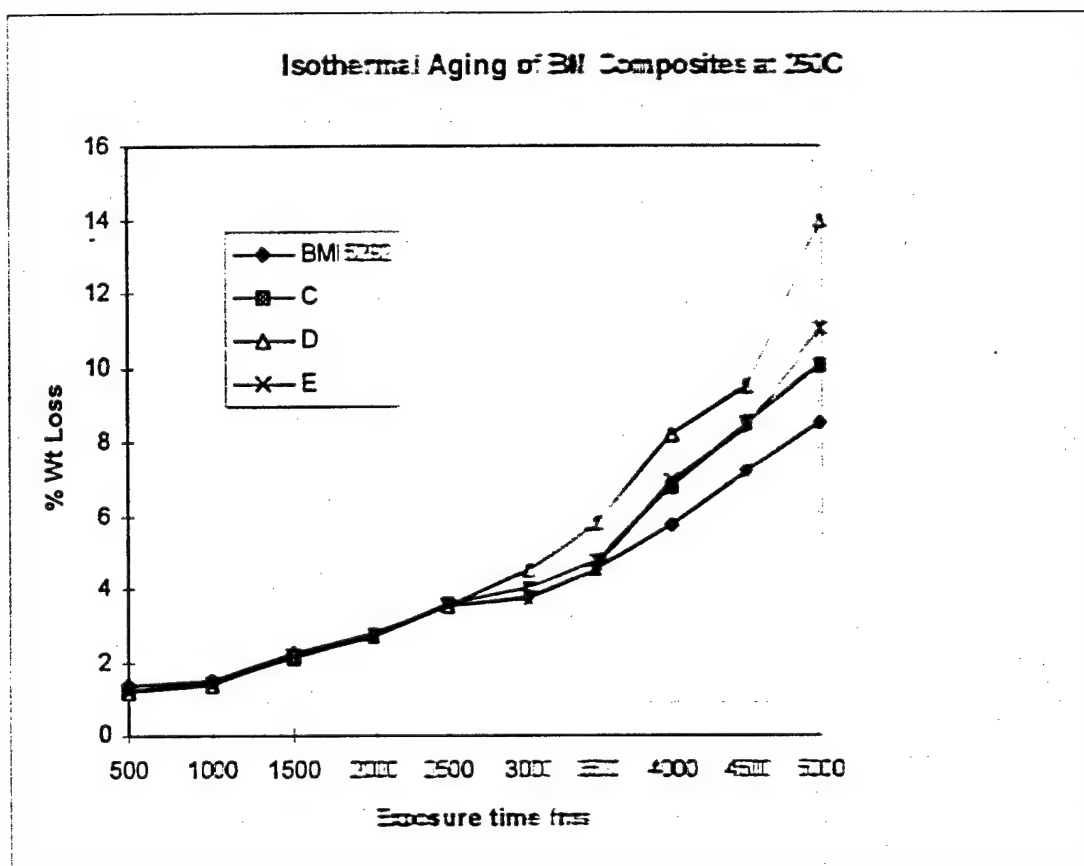


Figure 4. Isothermal Aging of BMI Composites at 260°C

Isothermal aging data showed that for the first 2500 hours there is no significant difference in weight loss among the various BMI microstructures. On longer aging times, the BMI with bulky substituents easily lost weight at a faster rate than the

baseline BMI 5292. The fact that laminate D, i.e. the BMI with the longest substituent, i.e. biphenyl, lost weight faster than laminate B (i.e. phenyl) and laminate E (i.e. naphthyl) led us to surmise that perhaps the substituents were being broken off, thus contributing to the overall increased weight loss. If this were the case, then the BMI matrices in which some substituents were broken off would have a network structure resembling that of the baseline BMI. One method to investigate this possibility is to measure the changes in glass transition temperatures by dynamic mechanical analysis.

Table I. Glass Transition Temperatures of Laminates (by DMA)

	Tg (initial), C	Tg (at 5000 hours), C
BMI 5292	290	260
Laminate C	310	270
Laminate D	340	265
Laminate E	320	270

The data show that the initial Tg for the substituted BMI matrices are higher than that for the baseline BMI 5292 due to their more bulky structures. However, at the end of 5000 hours, all laminates show similar glass transition temperatures, indicative of perhaps similar (degraded) network structures.

4. CONCLUSION

The network structures of bismaleimides can be modified by bulky substituents around the amic linkages. However, thermooxidative stability is not improved because of the tendency for the substituents to undergo scission from the main polymer backbone, reverting to the un-substituted network structure.

ACKNOWLEDGEMENT

This work is supported by the U.S. Air Force Office of Scientific Research under Contract F49620-95-C-0022.

REFERENCES

1. Bowles, K. J. and Meyers, A., in *Proc. 31st International SAMPE Symp. and Exhibition*, ed. J. L. Bauer and R. Dunaetz, Soc. for Adv. Mater. and Process Eng., Covina, CA, **1986**, p.1285.
2. Bowles, K. J. and Nowak, G., *J. Composite Materials*, **22** (1988) 966.
3. Bowles, K. J., *SAMPE Quarterly*, **24** (1993) 49.
4. C. L. Leung, R. Ghaffarian, and K. C. Leung, *Polym. Degradation and Stability*, in press.
5. G. F. L. Ehlers, K. R. Fish and W. R. Powell, *J. Polym. Sci.*, **A1(8)**, 3511 (1970).
6. H. H. G. Jellinek, *Polymer J.*, **4**, 489 (1973).
7. J. G. Calvert and N. J. Pitts., Jr., *Photochemistry*, Wiley, New York, 1966, Table A-5.
- ⁸C. F. Koelsch and S. J. Wawzonek, *J. Org. Chem.*, **6**, 684 (1941).
- ⁹E. K. Fields, S. J. Behrend, S. Myerson, M. L. Winzenburg, B. R. Ortega, and H. K. Hall, Jr., *J. Org. Chem.*, **55**, 5165 (1990).

APPENDIX C

Thermo-oxidative Stability of Polyimides: III. Effects of Polarity

Chuk L. Leung, and Kenneth C. Leung

PolyComp Technologies, Inc., Del Mar, CA 92014, USA

Abstract

Thermo-oxidative stability of polyimides under long-term isothermal exposure was studied. Model polyimides were prepared with novel chemical structures in which the polarities of the monomeric reactants were modified through the replacement of carbonyl functionalities. Results indicate that laminates made with these novel monomers exhibited less weight loss and decreased microcracking upon long-term isothermal aging.

Thermo-oxidative Stability of Polyimides: III. Effects of Monomeric Polarity

Chuk L. Leung, and Kenneth C. Leung

PolyComp Technologies, Inc., Del Mar, CA 92014, USA

1. INTRODUCTION

Polyimides are increasingly being used in high-temperature structural composites for airframe and engine applications. Various studies have been conducted in an attempt to quantify the isothermal aging effects on these polymer composites. Progress has been made in the understanding of the sample geometry¹, reinforcing fibers², and the temperature effects³ on the thermo-oxidative stability of the composite as a whole. However, there still exist a need for a systematic study that relates the phenomenological measurement of thermal stability with the chemical structure of the matrix polymers, which are the predominant failure sites, manifested by embrittlement, outgassing, weight loss and microcracking. A basic understanding of the structure-property relationship of polyimides will enable the intelligent selection and formulation of matrices that are thermally stable and would fulfill their mission requirements. Our approach aims at developing a understanding of the influence of polymer chemistry on composite stability by conducting novel polymer modifications and formulations to provide different polymer structures to minimize thermo-oxidative degradation of polyimides. In the previous papers^{4, 5}, we showed that while the network structure of polyimides can be strongly influenced by the molecular weights of the prepolymers, however the effect of bulky substituents in the vicinity of the amide linkage is negligible. In this paper, we

wish to report on the work on the effect of thermo-oxidative stability by modifying the polarities of the amide groups.

The generalized repeat structures of imides, as shown below, consist of two carbonyl functional groups on the furandione:

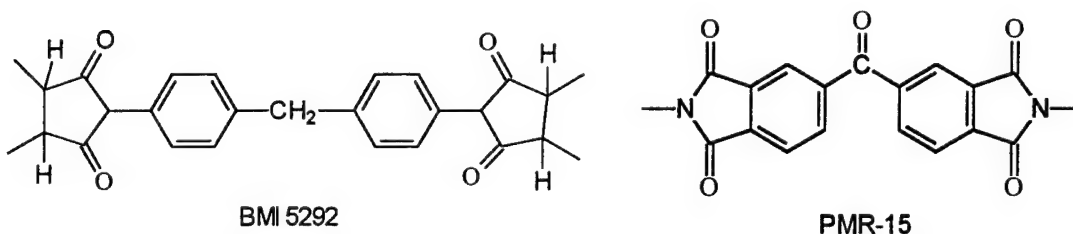


Figure 1. Repeat structures of polyimides

According to the stabilization mechanisms proposed by Frye and Horst⁶, and Kolesov *et al.*⁷, the replacement of labile groups with more stable groups near cleavage sites in the main chain should prevent initiation of chain breakage (the “weak bond” hypothesis”). It has also been commonly accepted that chemical reactions are strongly influenced by the polarity of the neighboring groups. We propose to extend this hypothesis to polyimides by modifying the bond strength of the amide linkage by replacing the highly polar carbonyl with non-carbonyl functionalities. The condensation between these monomers and diamine yield “imide analogs” that are heterocyclics that mimic the imide ring but without the usual arrangement of adjacent linkages that are susceptible to thermo-oxidative chain scission. The model compounds are shown in Figure 2 below.

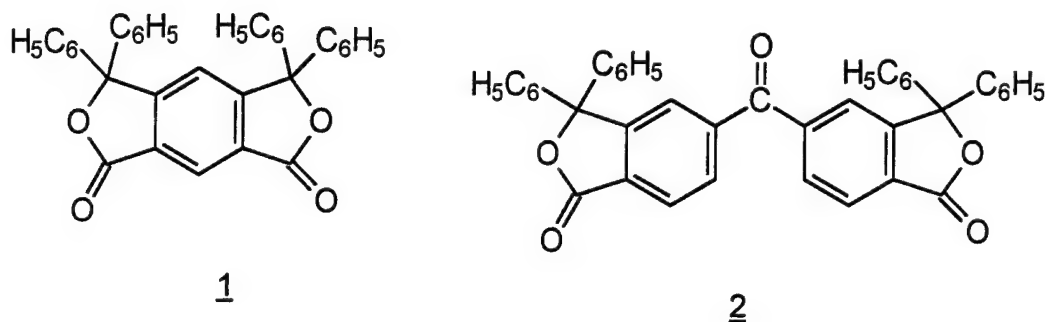


Figure 2. Model compounds for the preparation of polyimidines

2. EXPERIMENTAL

2.1 Synthesis of Monomers (1) and (2)

The synthesis of (1) and (2) involves the Friedel-Crafts reaction of pseudo acid chlorides have been described extensively by Ueda *et al.*⁸ and Cassidy *et al.*⁹,. Figure 3 shows the reaction paths for the synthesis of (1), for a yield of about 50%. Monomer (2) can be similarly synthesized by replacing 1,2,4,5-benzenetetracarboxylic dianhydride with 3,3',4,4'-benzophenonetetracarboxylic dianhydride at a lower yield (about 30%). These monomers were synthesized in the *cis* and *trans* isomeric forms, depending on their respective solubilities in 6M KOH¹⁰. Their melting points and elemental analysis are tabulated in Table I.

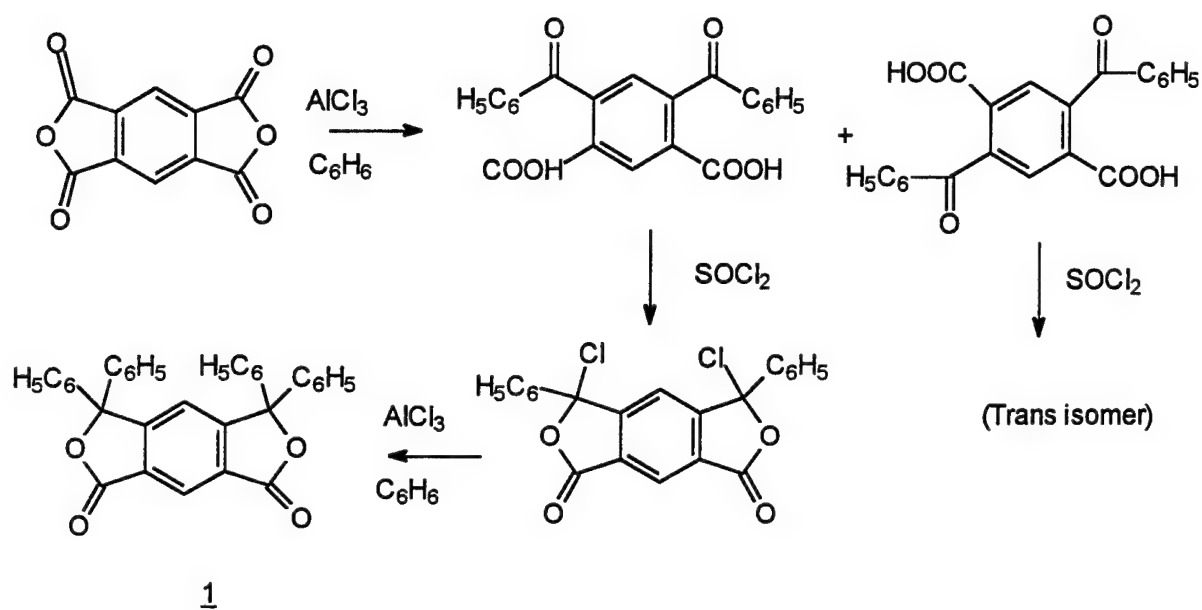


Figure 3. Synthesis of tetraphenylpyromellitimide as precursor for polyimidine

Table I. Melting Points and Elemental Analysis for Monomers 1 and 2

	Monomer (<u>1</u>)		Monomer (<u>2</u>)	
	cis	trans	cis	trans
m.p. °C (lit)	275	354	228	305
(found)	277	352	230	308
C-H (calc)	C 80.6, H 4.5	C80.6, H 4.5	C 82.3, H 4.4	C 82.3, H 4.4
(found)	C 80.5, H 4.5	C 80.7, H 4.5	C 82.4, H 4.3	C 82.4, H 4.3

In this work, we wish to investigate the effect of substituting the BTDA monomer in the PMR-15 polyimide formulation with the anhydride analogs 1 and 2 . Therefore, by using monomers BTDA, 1, 2, and PYRO (1,2,4,5-benzenetetracarboxylic dianhydride), polyimides of various structures were prepared as depicted in Figures 4 and 5. Monomers 1 and 2 exist in *cis* and *trans* isomeric forms, as shown previously. It is convenient for this work to overlook the effect of isomeric forms on the stability of the matrices. Therefore, equal amount of the *cis* and *trans* isomers for monomers 1 and 2 are used in each formulation

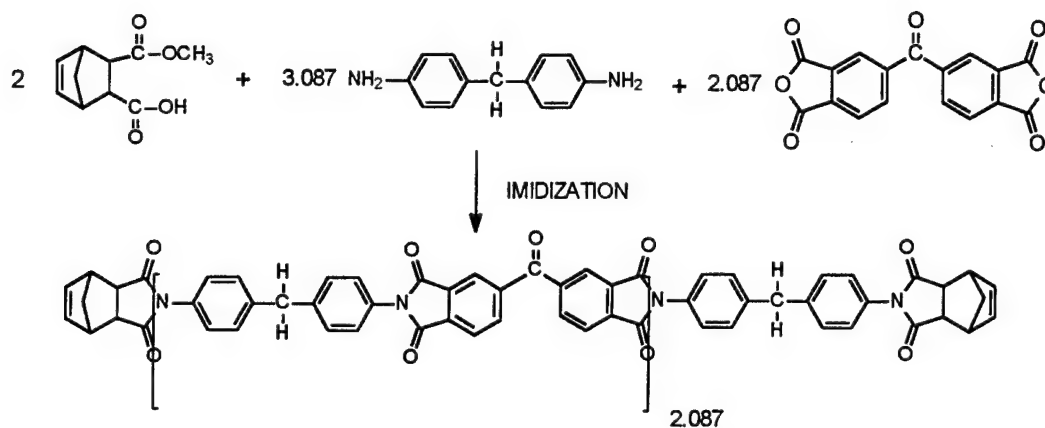


Figure 4. Polymerization of PMR-15 polyimide

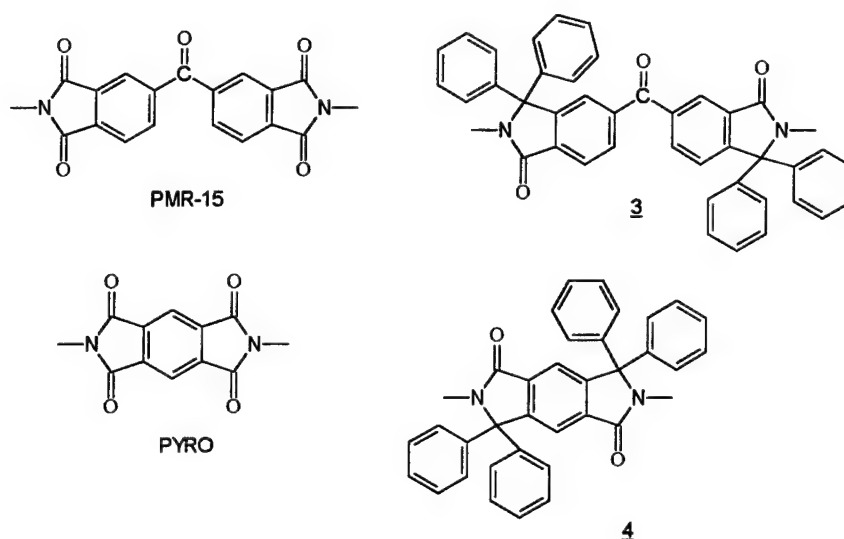


Figure 5. Polyimide structures

2.2 Neat Resin Polyimide and Water Diffusivity

Polyimide neat resin specimens were prepared by dissolving the respective reactants in dioxolane and evaporating the solvent, forming a dry powder containing nadic ester:diamine:dianhydride in the molar ratio of 2:3.087:2.087, as shown in Figure 4.

About 10 grams of each formulation were placed in the cavity of a stainless steel, take-apart matched-die mould (10 cm x 2 cm x 0.2 cm gap) and cured at a temperature of 315C for 18 hours under a pressure of 1.5MPa in a platen press. The mould was then removed from the press, and when still hot carefully taken apart to retrieve the specimen bar. The specimen bars were placed in a dessicator until ready for use.

Water absorption were measured by immersing pre-dried (at 100°C under full vacuum for 12 hours) specimen bars in water at 80°C and measuring the weights at regular intervals.

2.3 Prepregging and Laminate Cure

Prepregs were prepared by dissolving the respective monomeric reactants in N-pyrrolidone (NMP) and casting onto graphite fabric (8 harness satin, Celion® GC300500 from Fiberite Corp.) The solvent was allowed to evaporate, yielding prepregs with solid content of about 50%. Laminates were obtained by laying up 6-ply of the respective prepregs, each ply measuring 30 cm by 30 cm, placed in a vacuum bag and autoclave cured at 315°C and 1.5 MPa for 6 hours. The panels were then post-cured in an air-circulating oven at 315°C for an additional 12 hours. Specimens of dimensions 20 cm x 20 cm were cut from the panels and edge polished.

2.4 Isothermal Aging

Thermal exposure was carried out in an air-circulating Blue M oven at atmospheric pressure. Specimens, each measuring 20cm by 20 cm, were previously dried at 150°C for 24 hours before their initial weights were determined. The weighed panels were then arranged vertically in the oven, with care being taken to minimize dead-spots in air circulation. At pre-determined time intervals, the oven heater was turned off, and the temperature was allowed to return to ambient. The panels were then removed from the oven and stored in dessicators while waiting to be weighed.

3. RESULTS AND DISCUSSION

Monomers (1) and (2) are light yellow in color and are more soluble in common organic solvents. The resulting polyimidines are high temperature polymers, and the replacement

of one carbonyl with phenyl groups do not appear to change the glass transitions or water diffusivities, as shown in Table II.

Table II. Neat Resin Properties of Polyimides

	Tg (C)	WaterUptake at 80°C	
		Wt gain (%)	Diffusivity (mm ² /s)
PMR-15	343	4.2	2.5E-8
Polyimidine <u>3</u>	350	4.1	2.1E-8
PYRO	400	3.8	2.0E-8
Polyimidine <u>4</u>	410	3.7	2.1E-8

Figures 6-8 show the cross-sectional micrographs of the composites, showing that the polyimidines can be fabricated into high quality laminates with conventional polyimide cure cycles.

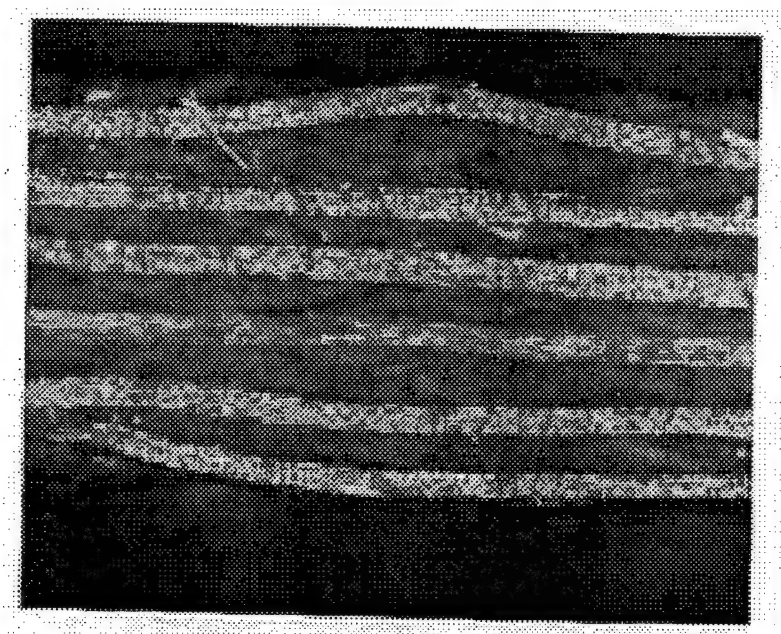


Figure 6. Cross-sectional (0°) micrograph of Polyimidine 3

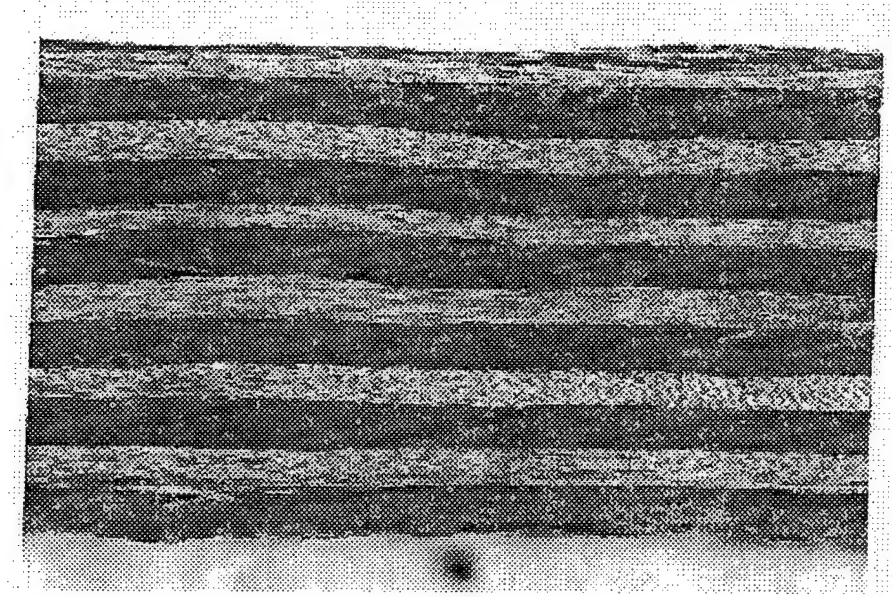


Figure 7. Cross-sectional (0°) micrograph of polyimide PYRO

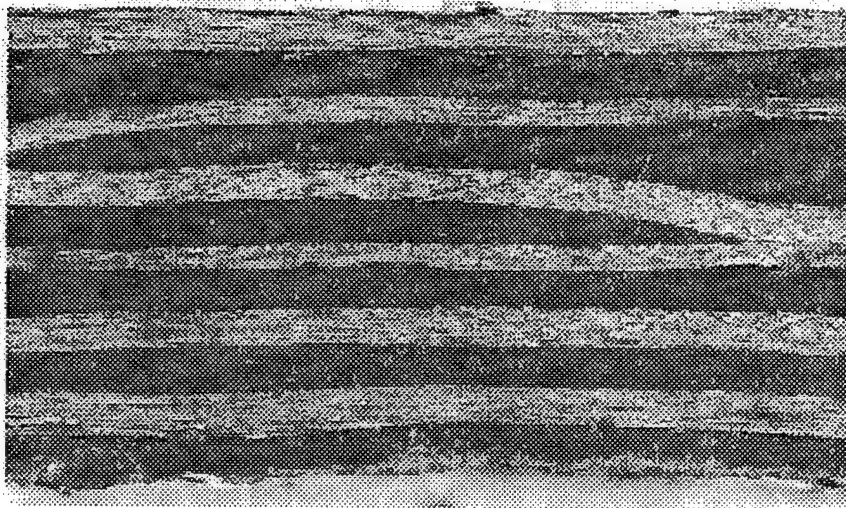


Figure 8. Cross-sectional (0°) photomicrograph of Polyimidine 4

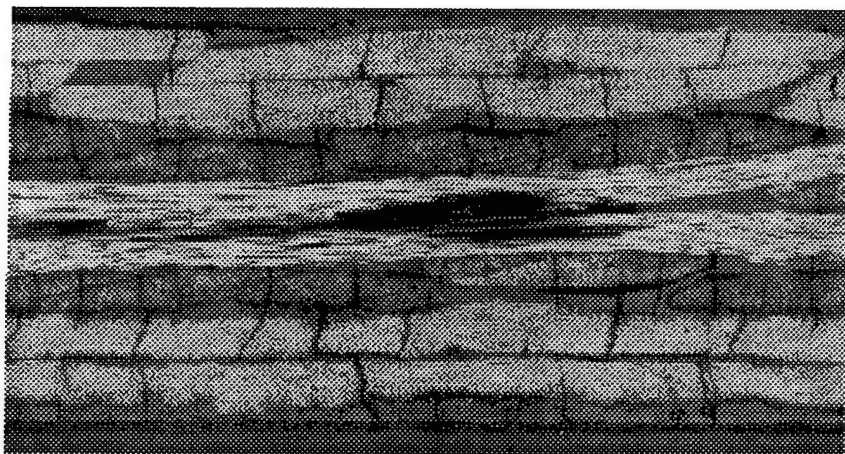


Figure 9. Cross-sectional (45°) photomicrograph of PMR-15 after 6000 hours at 260C



Figure 10. Cross-sectional (45°) view of Polyimide PYRO after 6000 hours at 260C



Figure 11. Cross-sectional (45°) view of Polyimidine 3 after 6000 hours at 260C



Figure 12. Cross-sectional (45°) view of Polyimidine 4 after after 6000 hours at 260C

The photomicrographs show that while all laminates microcracked after extended periods of isothermal aging, the extent of microcracking is less severe in the polyimidine laminates

Figures 9 and 10 shows the weight loss for the composite panels..

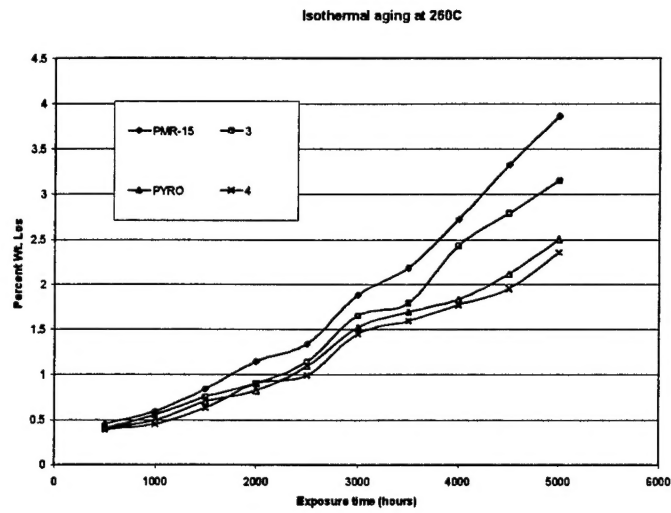


Figure 9. Isothermal aging of polyimide composites at 260C

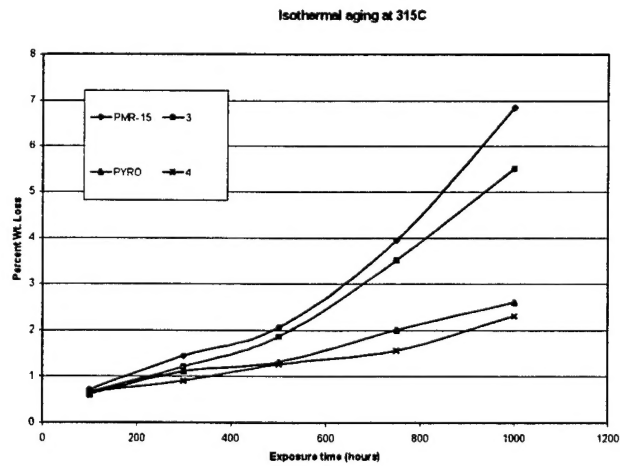


Figure 10. Isothermal aging of polyimide composites at 315C

The data show that within each group, decreasing the polarities of the imide bonds resulted in lower weight loss, perhaps indicating a decreased fragmentation of the polymer chain, resulting in decreased microcracking after thermo-oxidative aging. This appear to agree qualitatively with the bond strength calculation shown by Calvert and Pitts¹¹ that there is a increase in the strength of the bonds α to one of the carbonyl groups in the compounds shown in Figure 11. This would indicate that the polyimidines have a more stable amide bonds gthan the conventional polyimides, accounting for the isothermal aging results observed in Figure 9 and 10.

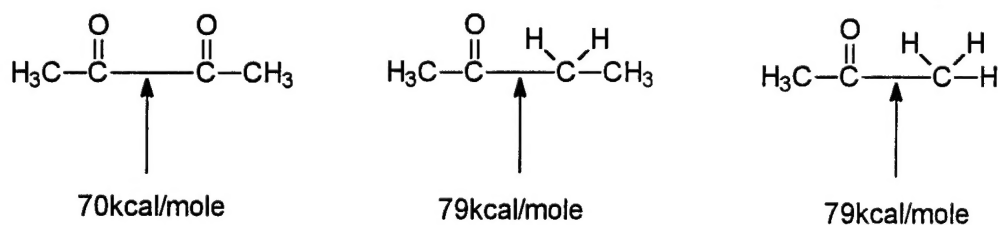


Figure 11. Examples of increases in bond dissociation energies by replacing adjacent carbonyl functionality

4. CONCLUSION

One of the main mechanisms for the thermo-oxidative degradation of polyimides is the dissociation of the amide bond, probably due to the high polarities of the adjacent carbonyl functionalities. We have shown that by replacing one of the carbonyls, we can reduce this polarity and improve the stability of the polyimide structure.

ACKNOWLEDGE

This work is supported by the U.S. Air Force Office of Scientific Research under Contract F49620-95-C-0022.

REFERENCES

1. Bowles, K. J. and Meyers, A., in *Proc. 31st International SAMPE Symp. and Exhibition*, ed. J. L. Bauer and R. Dunaetz, Soc. for Adv. Mater. and Process Eng., Covina, CA, 1986, p.1285.
2. Bowles, K. J. and Nowak, G., *J. Composite Materials*, **22** (1988) 966.
3. Bowles, K. J., *SAMPE Quarterly*, **24** (1993) 49.
4. C. L. Leung, R. Ghaffarian, and K. C. Leung, *Polym. Degradation and Stability*, **58**, 11-14 (1997).
5. C. L. Leung and K. C. Leung, *Polym. Degradation and Stability*, in press.
6. A. F. Frye and R. W. Horst, *J. Polym. Sci.*, **40**, 419 (1959).
7. S. V. Kolesov, a. A. Berlin, and K. S. Minsker, *Vysokomol. Soedin.*, **A19**, 381 (1977).
8. M. Ueda, M. Ohkura, and Y. Imai, *J. Polym. Sci., Poly. Chem. Ed.*, **12**, 719 (1974).
9. P. E. Cassidy and A. R. Syrinek, *J. Polym. Sci., Poly. Chem. Ed.*, **14**, 1485 (1976).
10. N. Fawcett, P. Cassidy, and J. Lin, *J. Org. Chem.*, **42**(17), 2929 (1977).
11. J. G. Calvert and N. J. Pitts, Jr., *Photochemistry*, Wiley, New York, 1966, **Table A-5**.